"LONGER-TERM" MERCURY EMISSIONS VARIABILITY FROM COAL-FIRED POWER PLANTS

Paul Chu
EPRI, 3412 Hillview Avenue, PO Box 10412, Palo Alto, CA 94303
Phone: (650) 855-2812; Fax: (650) 855-1069; pchu@epri.com

Ralph Roberson
RMB Consulting & Research, 5104 Bur Oak Circle, Raleigh, NC 27612
Phone: (919) 510-0376; Fax: (919) 510-5104; roberson@rmb-consulting.com

Dennis Laudal
Energy & Environmental Research Center, PO Box 9018, Grand Forks, ND 58202-9018
Phone: (701) 777-5138; Fax: (701) 777-5181; dlaudal@undeerc.org

Lynn Brickett
U.S. Department of Energy National Energy Technology Laboratory
PO Box 10940 MS 922-273C, Pittsburgh, PA 15236-0940
Phone (412) 386-6574; Fax: (412) 386-5917; brickett@netl.doe.gov

Wei-Ping Pan
Western Kentucky University, 1 Big Red Way, Bowling Green, KY 42101
Phone: (270) 780-2530; Fax: (270) 780-2569; wei-ping.pan@@wku.edu

ABSTRACT

To date, most mercury emissions data were developed using the Ontario Hydro method, which provides a "snapshot" of average mercury concentration over a 1-2 hour period. Since EPA is considering mercury CEMs for continuous monitoring and compliance, long-term mercury data are critical for power plants in order to understand the variability in mercury emissions, and the potential effects of plant operations on mercury. In order to characterize the variability in mercury emissions due to process and operating changes, such as coal and unit load, EPRI, DOE, and others conducted ~1 month studies to characterize longer-term mercury emissions from coal-fired power plants. Measurements were conducted at 16 different coal boilers, and evaluated a range of coal types (bituminous, sub-bituminous, as well as blends of lignite/Powder River Basin (PRB) and bituminous/PRB), boiler designs (cyclone, wall-fired, and tangential) as well as particulate (ESPs, fabric filters) and SO_2 (wet and dry) controls. The results were used to develop hourly and daily averages. For several of the power plants tested, the highest and lowest daily averages varied by a factor of about five, with hourly averages varying by over an order of magnitude. The level of variability appeared to be site-specific, and is likely dependent, in part, upon the coal supply. This paper will present the results of these studies, and evaluate the variability of mercury emissions.

INTRODUCTION

At the time EPRI embarked on this project, very little information existed with respect to how mercury emissions from coal-fired power plants varied with time. Almost all the knowledge concerning mercury emissions from coal-fired power plants was confined to the results obtained from short-term (generally two hours in duration), manual stack tests – generally conducted in triplicate. These test results shed little light on how mercury emissions vary with time. Emission variability is important from several perspectives. First, it is important with respect to design and specification of control technology. Emission variability also has important regulatory consequences.

Regulatory Overview

On December 20, 2000, EPA published a finding in the Federal Register that the Agency intends to propose regulation to reduce mercury emissions from coal-fired electric utility steam generating units. EPA also stated that it intends to propose regulations for utility units under Section 112(d) of the Clean Air Act – usually referred to as MACT standards.

From time to time, regulatory agencies are faced with a situation in which a continuous method for monitoring emissions from a source becomes available long after a standard based on periodic test data has been established. Such may be the case with the utility MACT since EPA has indicated it will use the manual test data to set MACT limits, but is considering mercury monitors for compliance determinations. Agencies can convert a "periodic" standard to a "continuous" standard by adjusting the averaging time or by providing for de minimis relief periods during which excursions above the standard are excused. In making this conversion, agencies recognize that the stringency of an emission limit is determined not just by the numerical value of the standard but also by the averaging time associated with the numerical limit and the method used to make emission measurements.

Project Approach

Until EPRI initiated this project, the largest mercury emission dataset were the Part III results from EPA's Information Collection Request (ICR).[1] Building on previous EPRI and DOE research on the effect of selective catalytic reduction (SCR) on mercury[2], this project obtained mercury data using continuous mercury monitors (CMM) at as many sites as practicable. Data from R&D on activated carbon injection were generally short-term in nature, hours to days, and thus did not characterize long-term mercury emissions. In general, the approach was to set up CMMs in the stack or the particulate control device outlet for plants with wet FGDs because early on wet stacks were considered to be problematic to operate for extended test periods. We have since conducted one extended measurement at a wet stack. Manual mercury testing were conducted using the generally accepted "gold-standard", the Ontario Hydro (OH) mercury method in order to confirm the CMM results.

Two different CMMs were used for these tests: the PS Analytical (PSA) Sir Galahad and Tekran. These instruments, when used in conjunction with the Energy & Environmental Research Center (EERC) or PSA conversion systems, were able to measure total and elemental mercury. The

PSA Sir Galahad and the Tekran are based on the principle of atomic fluorescence (AF), which provides an inherently more sensitive signal than atomic absorption (AA). The systems use a gold-impregnated silica support for preconcentrating the mercury and separating it from potential interferences that degrade sensitivity.

These CMMs require a "conditioned" flue gas sample. Figure 1 illustrates the EERC pretreatment system used with CMMs. AF-type systems can directly analyze only Hg^0. Therefore, all mercury forms in the flue gas must be converted to Hg^0 using $SnCl_2$ as the reductant. To measure only Hg^0, the $SnCl_2$ is bypassed, and the Hg^{2+} concentration is calculated by difference. Because both Hg^{2+} and Hg^0 collect on the trap, the Hg^{2+} must be removed from the gas stream using either a heated carbonate trap (the EERC system) or a basic $SnCl_2$ trap (PSA system). The pretreatment/conversion system also removes gaseous contaminants (HCl, SO_3, etc.) from the flue gas, to prevent poisoning of the gold collection trap.

The conditioned gas sample is pumped through a gold trap, which is maintained at a constant temperature. The gold trap is flushed of any flue gas that may be present, before the mercury is desorbed by heating. The mercury is carried into the fluorescence detector by argon or nitrogen. The gold trap is then cooled in preparation for the next sample. The time for the entire process is about 5 min.

The systems are calibrated using Hg^0 as the primary standard. Typically, the calibration of these units has proven to be stable over a 24-hr period.

Description of the Power Plants and Coal

The units tested ranged from 150 to 1300 MW in size. The coals burned included twelve eastern bituminous coals, two lignite/Powder River Basin (PRB) coals, one PRB/eastern bituminous blend, one subbituminous coal, and one western bituminous coal. The plant configurations of air pollution control devices included SCRs, electrostatic precipitators (ESPs), low NO_x burners (LNB), wet flue gas desulfurization (FGD), combination SO_2/particulate scrubber, fabric filters and spray dryer/fabric filters. For the purposes of this paper and for continuity with previous Hg projects, the plants utilized during SCR testing are referred to as Sites S2, S4, S5, and S6; the plants utilized for long term Hg testing (only) are referred to as Sites L1, L2, L3, and L4. Site L3 is still on-going and only limited results are presented comparing the side-by-side CMM comparison. Additional secondary identifiers include for sites were multiple units were tested, and include a unit identification (U-"plant number") or if applicable the sampling location in relationship to an ESP.

Table 1
Characteristics of the Units Participating in EPRI's Continuous Mercury Monitoring Program

EPRI ID	Unit No.	Coal Type	NOx Control	SO_2 Control	PM Control	Sampling Location
L2-U1	1	Lignite/PRB blend	LNB	Fuel Sulfur	Fabric Filter	Fabric Filter Outlet
L2-U3	3	Lignite/PRB blend	LNB	Wet FGD	ESPc	ESP Outlet
L1-U1	1	E. Bituminous	LNB	Fuel Sulfur	Fabric Filter	Fabric Filter Outlet
L1-U7	7	E. Bituminous	LNB	Fuel Sulfur	ESPc	Stack
S2	2	E. Bituminous	SCR	Wet FGD	ESPc	ESP Outlet
S4	1	E. Bituminous	SCR[1]	Combined SO_2/PM Scrubber		APH Outlet
S5-U1	1	E. Bituminous	SCR	Wet FGD	ESPc	ESP Outlet
S5-U3	3	E. Bituminous	LNB	Wet FGD	ESPc	ESP Outlet
S6-U1	1	E. Bituminous	SCR	Fuel Sulfur	ESPc	Stack
S6-U2	2	E. Bituminous	SCR[2]	Fuel Sulfur	ESPc	Stack
S6-U4	4	E. Bituminous	LNB	Fuel Sulfur	ESPc	Stack
S7	1	E. Bituminous	SCR	Spray Dryer / Fabric Filter		Stack
L3-Inlet	1	E. Bituminous	LNB	Fuel Sulfur	ESPc	ESP Inlet
L3-Outlet	1	E. Bituminous	LNB	Fuel Sulfur	ESPc	ESP Outlet
L4-Inlet	1	Subbituminous	LNB	Spray Dryer / Fabric Filter		SD Inlet
L4-Stack	1	Subbituminous	LNB	Spray Dryer / Fabric Filter		Stack
L5-FF Outlet	1	W. Bituminous	LNB	Wet FGD	Fabric Filter	Fabric Filter Outlet
L5-Stack	1	W. Bituminous	LNB	Wet FGD	Fabric Filter	Stack
L6	1	PRB/E. Bituminous Blend[3]	None	Fuel Sulfur	ESPc	ESP Outlet

[1] Approximately 50% of the data was collected before the beginning of the ozone season, and 50% with the SCR in operation.

[2] Tests were conducted with the SCR bypassed.

[3] Three different blend ratios were tested.

Table 2
Average Coal Characteristics During Monitoring Program

EPRI Site ID	Moisture, %	Ash, %	Sulfur, %	Heating Value, Btu/lb	Chlorine, ppm (dry)	Mercury, ppm (dry)
L2	31	16.6	0.5	6,413	30	0.32
L1	7.4	11.8	1.3	11,891	950	0.14
S2	6.1	9.4	3.9	12,096	450 – 690	0.14
S4	7.4	8.5	2.9	11,634	225 – 810	0.14
S5	4.6	12.1	3.6	11,835	430 – 500	0.14
S6	6.5	11.5	1.1	12,193	635 - 1,520	0.07
S7	8.3	8.2	0.95	12,649	1330	0.07
L4	27	5.0	0.3	8,595	10	0.067
L5	7.2	10.3	0.6	11,624	215	0.033
L6[1]	23.6 – 26.0	3.9 – 5.3	0.4 – 1.0	9078 – 9744	18 – 241	0.048 – 0.071

[1] Three different blend ratios were tested. Ranges are provided.

CMM Data Screening

A preliminary evaluation of the CMM data was conducted to identify problematic issues with the CMM data. Of primary concern was the inclusion of data during periods of CMM calibration, maintenance or malfunction, elemental Hg measurements, and outliers. Outliers were excluded if an individual CMM value was greater than 200% of the hourly average - one-half hour worth of data on each side of the sample point.

After being quality assured, the data were reduced to 1-hour and 24-hour averages. Since the testing protocol required periodic maintenance, calibration and twice daily Hg speciation to be performed, continuous Hg monitoring could not always be achieved. Coupled with occasional CMM malfunction, data gaps ranging from several minutes to several hours where observed. Additionally, varied sampling times were utilized by the various CMMs. An averaging convention was necessary to address the different sampling times and the different missing data regimes. The project team decided upon the following criteria for valid hourly and daily averages.

- Hourly averages must contain a minimum of 30 minutes of valid CMM readings
- Daily averages must contain a minimum of 12 valid hourly averages

Statistical analyses were conducted using all valid hourly averages and all valid daily averages. As a result, hourly averages not associated with daily averages were included in the final results.

Once the CMM data were quality assured, we computed hourly and daily averages. These results are plotted in Figure 2, with the hourly averages plotted as points, and the daily averages plotted as horizontal lines. Figure 2 indicates that there is significant variability in mercury emissions, not only on an hourly basis but also on a daily basis.

A cumulative frequency distribution plot (Figure 3) is also helpful in quantifying what percent of the time a unit emits at or below a given concentration. The cumulative frequency distribution plots show that while most units operate with periods with low concentrations, there is a percent of time when emissions concentrations are much higher than say the mean.

The data screening procedure is discussed in more detail in an earlier paper[3].

Overall CMM Data Evaluation

Table 3 provides a statistical summary of the CMM data for all the EPRI test sites. For this paper, mercury concentrations are reported in the units of $\mu g/m^3$. For a bituminous or subbituminous coal, 1 $\mu g/m^3$ at 7% O_2 converts to 0.92 $lb/10^{12}$ Btu. Hourly mercury emissions are quite variable, with the hourly relative standard deviations (RSDs) ranging from about 8 percent to more than 60 percent. Relative standard deviation is defined as the standard deviation of a dataset divided by the mean. With the exception of Site S6-U4, all of the bituminous coal-fired units have RSDs > 25 percent. The smallest RSDs are for the one unit (Site L4) that burns subbituminous coal. While increasing the averaging time from hourly to daily tends to "smooth" the data, it is important to note that the variability is still quite significant. Note that in Table 3 the mean of the hourly averages often is not equal to the mean of the daily values. As noted earlier, hourly averages not associated with daily averages were included in the final results.

Another means of quantifying variability is to compute upper and lower confidence intervals. Table 4 presents upper and lower 95 percent confidence intervals for both hourly and daily averages. From the perspective of complying with an emission limitation, the upper confidence interval is much more meaningful than the lower confidence interval. The mean is a quantity that the individual values exceed 50 percent of the time and likewise are less than 50 percent of the time. On the other hand, there is a 95 percent probability that an individual value will be less than the upper 95 percent confidence interval.

Table 3
Statistical Summary of EPRI CMM Data

		Hourly Averages		Daily Averages	
EPRI Site	**Coal Type**	**Mean, μg/m³**	**RSD[1], %**	**Mean, μg/m³**	**RSD, %**
L2 – U1	Lignite/PRB	34.3	18.5	34.7	12.7
L2 – U3	Lignite/PRB	16.9	24.8	16.7	17.4
L1 – U1	Bituminous	2.6	62.3	2.7	46.6
L1 – U7	Bituminous	6.9	30.1	6.6	31.4
S2	Bituminous	4.7	47.3	5.1	40.9
S4	Bituminous	6.1	27.4	6.0	21.0
S5 – U1	Bituminous	5.4	47.8	5.3	29.5
S5 – U3	Bituminous	5.9	59.0	6.5	32.1
S6 – U1	Bituminous	5.2	30.8	5.3	22.6
S6 – U2	Bituminous	5.8	42.9	5.6	18.7
S6 – U4	Bituminous	7.5	12.8	7.4	8.1
S7	Bituminous	0.1	123	0.1	107
L4 - Inlet	PRB	9.5	14.2	9.5	9.1
L4 - Stack	PRB	10.0	8.8	10.0	4.7
L5 – FF Outlet	W. Bituminous	0.18	59.3	0.18	45.8
L5 - Stack	W. Bituminous	0.05	33.7	0.05	12.9

[1] RSD stands for relative standard deviation, which equals the standard deviation of the data divided by the arithmetic average (mean).

Table 4
Summary of CMM Confidence Intervals

		Hourly Averages		Daily Averages	
EPRI Site	**Coal Type**	**LCI (95%), $\mu g/m^3$**	**UCI (95%), $\mu g/m^3$**	**LCI (95%), $\mu g/m^3$**	**UCI (95%), $\mu g/m^3$**
L2 – U1	Lignite/PRB	22.8	49.9	26.7	44.4
L2 – U3	Lignite/PRB	9.9	26.9	11.5	23.6
L1 – U1	Bituminous	0.4	9.4	0.9	6.4
L1 – U7	Bituminous	3.1	14.0	3.3	11.9
S2	Bituminous	1.5	11.3	2.0	10.9
S4	Bituminous	3.3	10.3	3.7	9.3
S5 – U1	Bituminous	1.7	13.9	2.6	9.7
S5 – U3	Bituminous	0.7	28.3	3.4	11.5
S6 – U1	Bituminous	2.5	9.8	3.3	8.2
S6 – U2	Bituminous	2.6	11.1	3.7	8.1
S6 – U4	Bituminous	5.8	9.6	6.3	8.7
S7	Bituminous	-0.1	0.3	-0.1	0.3
L4 – Inlet	PRB	6.7	13.0	7.9	11.4
L4 - Stack	PRB	8.3	11.9	9.1	10.9
L5 – FF Outlet	W. Bituminous	0.0	0.4	0.0	0.4
L5 - Stack	W. Bituminous	0.0	0.1	0.0	0.1

"Low-Level" Mercury Measurements

EPRI was particularly interested in characterizing variability from units with relatively low mercury emissions. After all, these are the types of facilities that EPA is required to consider in developing MACT floors. Measurements were conducted at two power plants – Sites S7 and L5. These two sites were selected because both exhibited low mercury concentrations when tested in 1999 pursuant to EPA's mercury information collection request (ICR).

The results are summarized, along with the other test sites, in Tables 3 and 4. For Sites S7 and L5, mercury emissions were often below detection limits of the Ontario Hydro method and detection limits for the CMM measurements have not been formally established. Thus, we must

question the absolute accuracy of all of these mercury measurements. Our conclusion is that mercury emissions from these two sites are consistently less than 0.5 $\mu g/m^3$, however we question whether the concentrations are truly as low as 0.05 $\mu g/m^3$. This question can only be answered with additional research.

Analysis of EPRI's CMM dataset suggests, even at these low levels, there is considerable temporal variability in mercury emissions from coal-fired utility boilers. The cumulative frequency distribution plots (e.g. Figure 3) of the hourly average mercury concentrations are quite consistent across the test locations. This observation suggests there is similarity in the form of the distributions. The cumulative frequency distribution plots are also helpful in quantifying what percent of the time a unit emits at or below a given concentration. The cumulative frequency distribution plots show that while most units operate with periods with low concentrations, there is a percent of time when emissions concentrations are much higher than say the mean. In other words, mercury emission concentrations vary with time.

"Precision" Tests

One curious phenomenon of the CMM data are spurious spikes that sometimes appear in the data. In this context, a "spurious spike" is defined as a single measurement period (typically 2.5 – 5 minutes in duration) for which the apparent mercury concentration increases by a factor > 2 from the preceding measurement. As noted earlier, these spikes were considered outliers and not included in the data analyses. To evaluate whether these spikes were real, i.e. represented true flue gas concentrations, two side-by-side CMM systems were operated at the same location at two coal-fired power plant. An example of the results from this side-by-side comparison is shown in Figure 4. The spikes do not appear to represent the bulk flue gas mercury concentration, but likely represent actual mercury emanated from the coal. The spikes likely result from a sudden release of accumulated mercury within the CMM system.

The variability in the CMM data includes both sampling/analytical variability and process variability. A possible source of this sampling and analytical variability is the flue gas pretreatment system, which converts the oxidized mercury to elemental mercury, as well as removes contaminants such as SO_3 and HCl. The test coal was a blend of PRB and eastern bituminous coal at Site L6. Results from precision tests conducted while burning a medium-sulfur, high-Cl coal[3] also indicated similar spikes, although one CMM indicated much more variability - standard deviation of 3.9 $\mu g/m^3$ as compared with 0.4 $\mu g/m^3$. However, the means (of all the data) were relatively consistent - 4.7 $\mu g/m^3$ and 5.0 $\mu g/m^3$, respectively.

The results indicate the potential sampling/analytical variability about the CMM; however our belief is that future CMMs will evolve away from the current wet chemistry pretreatment systems to more operator-friendly dry-based systems.

Summary and Conclusions

Until EPRI initiated this project, the largest mercury emission dataset were the Part III results from EPA's ICR. As a crude means of comparison, the ICR dataset consists of approximately 80 units x 3 test runs x 2 hours/run ~ 480 unit operating hours. On the other hand, the new CMM

dataset contains about 5000 operating hours of data across the various sites summarized in this paper. Thus, our first conclusion is that this should be an important and meaningful mercury dataset.

Analysis of the CMM dataset demonstrates that there is considerable temporal variability in mercury emissions from coal-fired utility boilers. This variability consists across all coal ranks and unit configurations tested, including the two sites with emissions less than 0.5 $\mu g/m^3$. There does appear to be less variability for the one subbituminous test site (i.e., Site L4) – although more data are needed to fully evaluate this.

Two side-by-side "precision" measurement indicates potential variability due to the sampling and analysis system. A possible source of this variability is in the pretreatment system, as the flue gas is conditioned before the analyzer.

Data Gaps and Future Work

Additional long-term mercury measurements are necessary (and are planned) to better characterize the follow power plant configurations:

1. Downstream of an wet FGD including the combination of an SCR and wet FGD,
2. Blends of PRB and bituminous coal – do mercury emissions behave like a PRB or a bituminous coal, or some interpolation of the two coals, and
3. Additional low-rank coals, especially sub-bituminous to evaluate whether the lower rank coals yield less variable mercury emissions.

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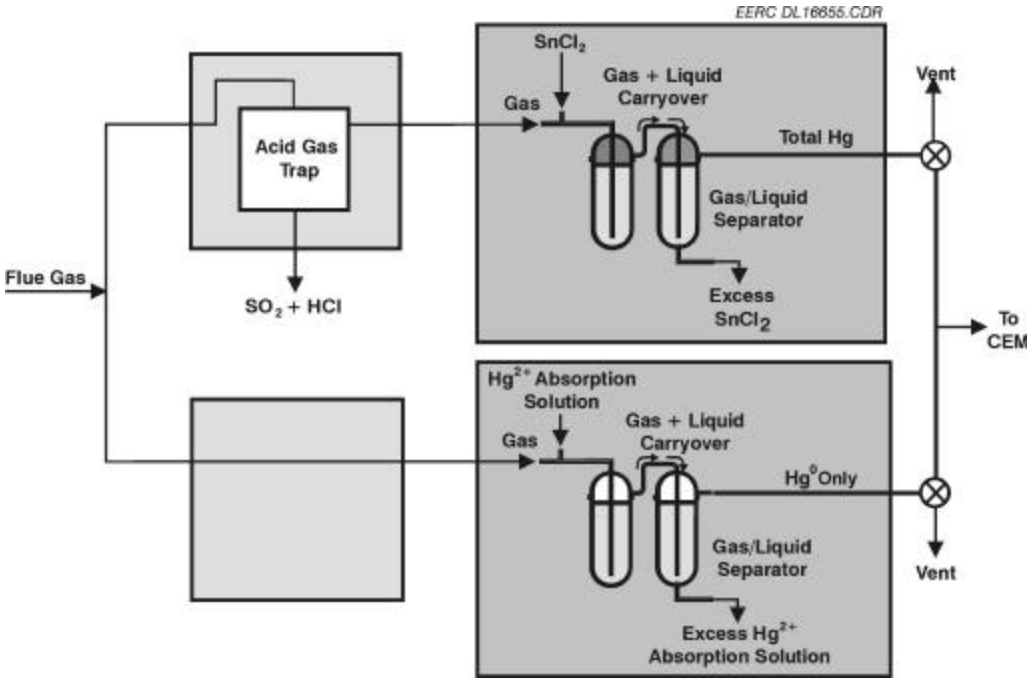

Figure 1 - Schematic of the EERC Pretreatment/Conversion System for Use with CMMs

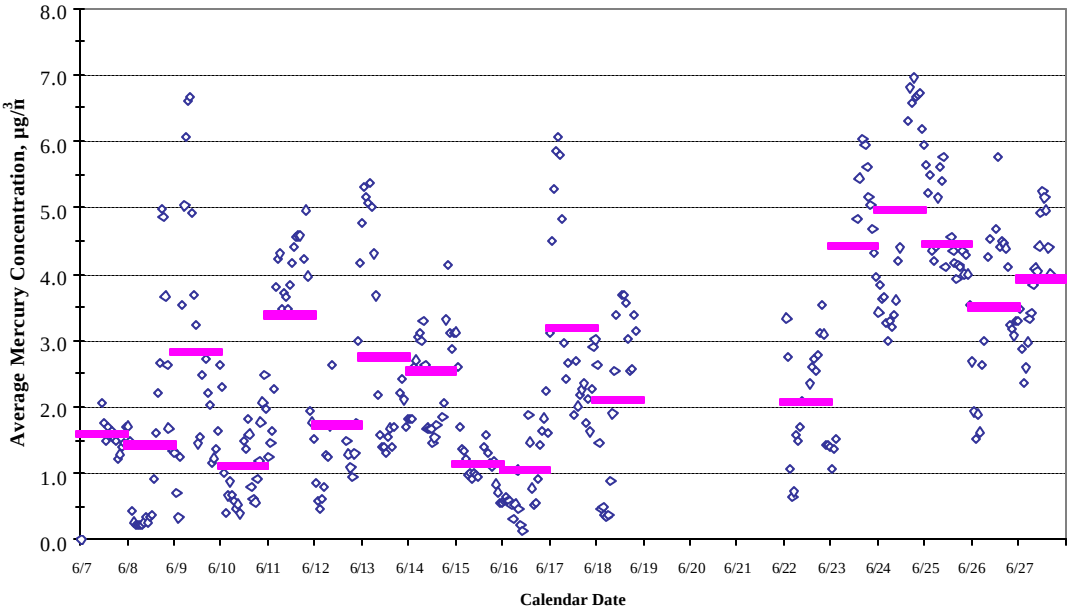

Figure 2 – Comparison of Hourly and Daily Averages for Site L1-U1

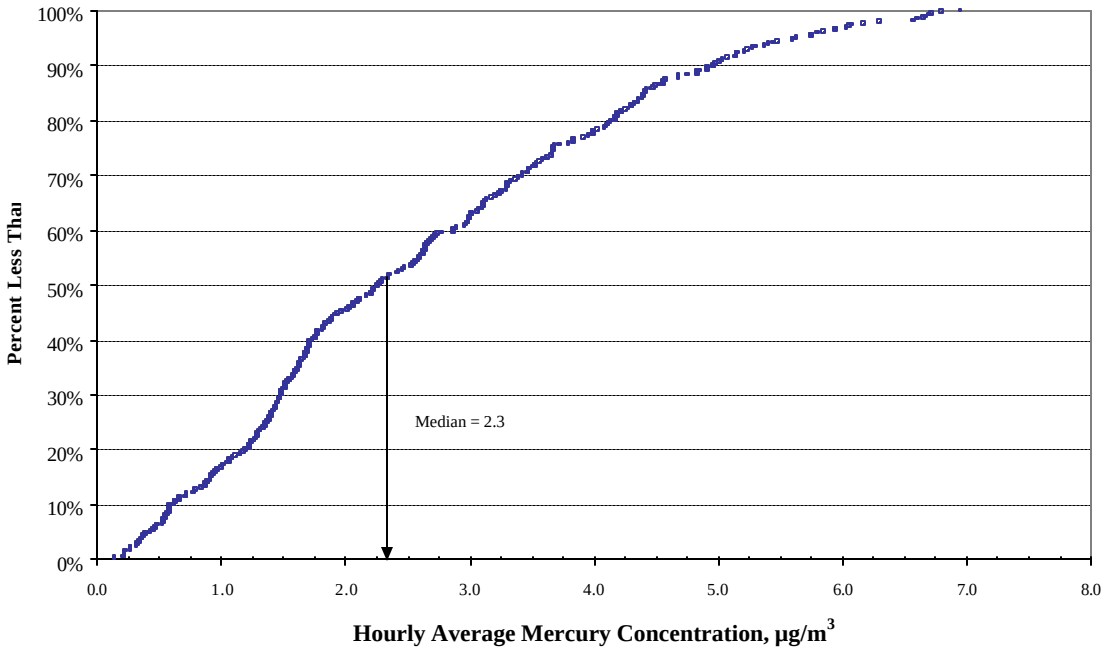

Figure 3 – Cumulative Distribution Plot for Site L1-U1

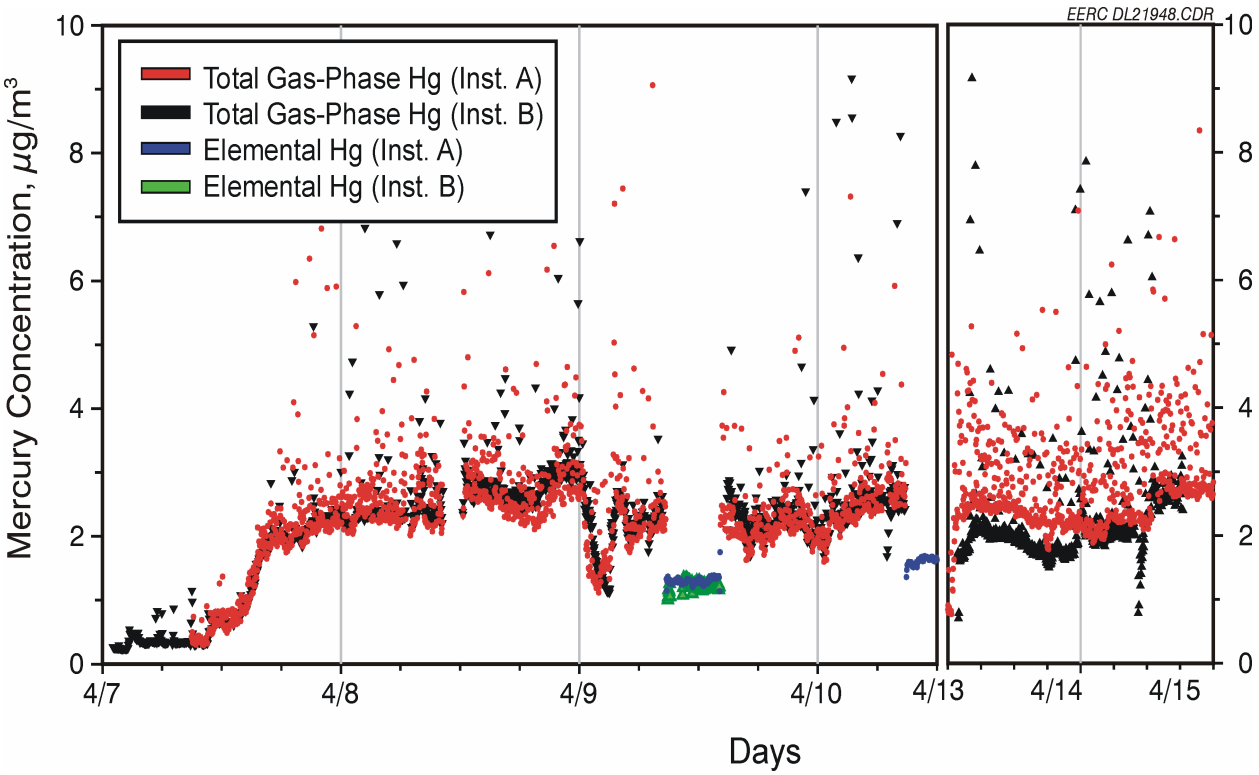

Figure 4 – Side-by-side "Precision" CMM Measurements at Site L6 burning 85/15 (up to 4/13) and 70/30% (after 4/13) PRB/E. Bituminous